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Synthesis of H_2SO_4 doped polyaniline film by potentiometric method

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Abstract. **H_2SO_4 doped polyaniline films were synthesized in aqueous acidic media. The polyaniline film deposited on platinum electrode exhibits highest conductivity. The conductivity of each H_2SO_4 doped polyaniline sample was determined by the four-probe technique. The current–voltage curve exhibits that polyaniline sample has an ohmic behaviour. Experiments were conducted to establish the conductivity of the sample from room temperature to 110°C. The current was set constant. It has been observed that at lower current as well as higher current conductivity of the polyaniline sample is due to the electrons transferred to the conduction band. It is observed that the concentration ratio of 0·2 : 1 of aniline and H_2SO_4 for synthesis of PANI film on platinum electrode shows good conductivity.**

Keywords. **Aniline; electrolytes; electrochemical polymerization; four-probe technique.**

1. Introduction

In the earlier days, all carbon-based polymers were treated as an insulator. However, in later phase, it has been proved that different polymers and their derivatives can undergo transition from insulator to semiconductor when doped with oxidizing or reducing agent (Kobayashi *et al* 1984; Kadirgan 1998; Abdiryim *et al* 2005). Polymer films, known as polymer modified electrodes, with metal particles were incorporated into the films either during film formation or electrodepositing onto the polymer films. Polyaniline have certain advantages over other conducting polymers, including simplicity and rapidity of preparation by electrochemical methods, and the ability to be formed in aqueous electrolytic solutions (Diaz and Logan 1980; Oshaka *et al* 1984; Gerard *et al* 2002). The polyaniline (PANI) is one of the most studied conducting polymers, not only due to the facility in preparation procedures, but also related to high stability to the environmental exposition. The normal polymerization to prepare for the emeraldine form, and its protonation (doping) and many other physical–chemical properties are connected to the presence of the NH group (Kang *et al* 1998). Polyaniline is composed of aniline repeat units connected to form a backbone of alternating nitrogen and benzene rings. It exists in a variety of forms that differ in chemical and physical properties. It also comes in three classifications depending upon the degree of oxidation of the nitrogen atoms: the leucoemeraldine base (LEB), emeraldine base (EB) and pernigraniline base (PNB) as shown in figure 1.

Four-probe method permits measurements of the resistivity in the samples having wide variety of shapes, including the resistivity of small volume within bigger semiconductor. The present work deals with the conductivity measurements of the H_2SO_4 doped polyaniline film sample with varying temperature at constant current, I. Polyaniline sample is known to be classified as a combination of EB and LB. Four-probe method is employed in the present investigation.

Polyaniline class of conducting polymer has been widely investigated aiming towards potential applications for rechargeable batteries, protection coating, electrochromic displays, conducting composite material, gas sensor, corrosion protection, electronic, biosensors and optical devices (Borole *et al* 2004; Gerard and Malhotra 2005).

2. Experimental

H_2SO_4 doped films were synthesized by electrochemical polymerization of aniline on platinum substrate under potentiometric conditions at room temperature using indigenously developed electrochemical polymerization system. The electrolyte cell consists of platinum based working and counter electrode and a saturated calomel reference electrode was used. Aniline was distilled twice before use. The electrolyte was prepared using de-ionized water at room temperature. The aniline monomer with different concentrations (0·1 M, 0·2 M, 0·3 M, 0·5 M) was used. Three electrolytes H_2SO_4, HCl and HNO_3 were used for investigation. Three different concentrations of H_2SO_4 (0·5 M, 1 M, 1·5 M) were studied. After deposition, the working electrode was removed from the electrolyte and washed with supporting electrolyte solution. The polyaniline film

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samples were characterized by four-probe technique (Sari *et al* 2002; Hansen *et al* 2003).

The four-probe set up (Model DRF-02 Owen 1038-Optochem. International, New Delhi) was used for the conductivity measurement as illustrated in figures 2 and 3. A nominal value of probe spacing, which was found satisfactory, was at an equal distance of 2·0 mm between adjacent probes. They permit measurement with reasonable current of *n*-type or *p*-type semiconductors.

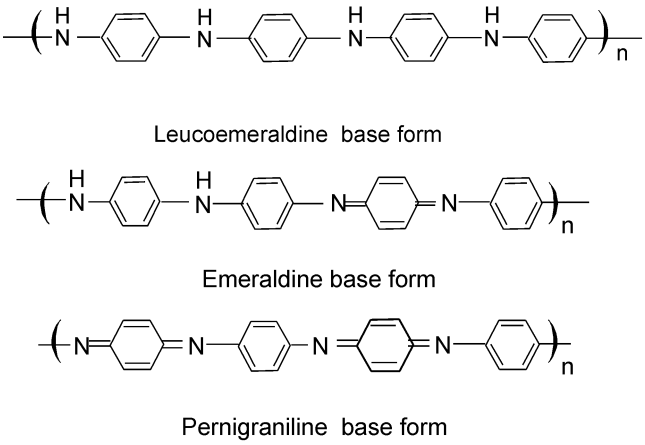

Figure 1. Chemical structure of polyaniline.

Figure 2. The four-probe apparatus and its accessories.

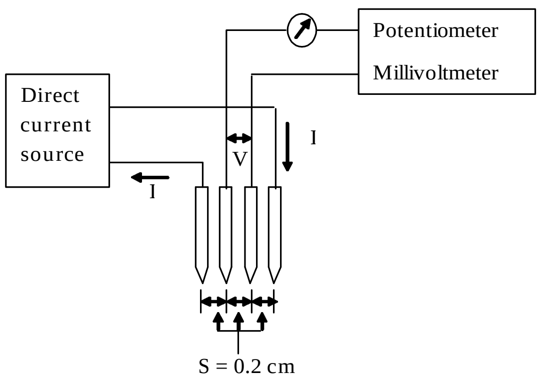

Figure 3. Schematic diagram of the four-probe apparatus.

The current, *I*, was set to a constant and the temperature was varied from room temperature to 110°C. The voltage was recorded with increasing temperature with an interval of 5°C. The resistivity was calculated at different temperatures using the following relationship

$$r = \frac{1}{G_7(W/S)} \times \frac{V}{I} \times 2p\,S,$$

where *S* is the distance between two probes, *W* the thickness of the sample, *I* the current flowing between the outer two probes, *V* the measured voltage between centre two probes, G_7 the correction factor and *r* the resistivity.

$$G_7(W/S) = \frac{2S}{W}\log_e 2.$$

Conductivity can be computed using the relationship, $s = 1/r$, where *s* is the conductivity, and *r* the resistivity of the sample.

3. Results and discussion

It has been reported that the conducting polymer based biosensors have a good operational stability, long storage

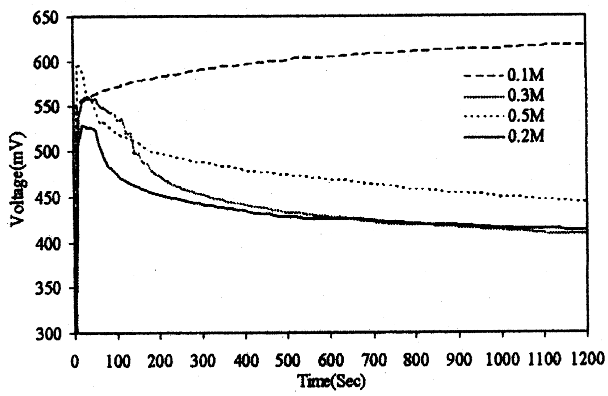

Figure 4. Chronopotentiogram recorded during electrochemical polymerization of different concentrations of aniline (0·1 M, 0·2 M, 0·3 M, 0·5 M) and 1 M of H_2SO_4.

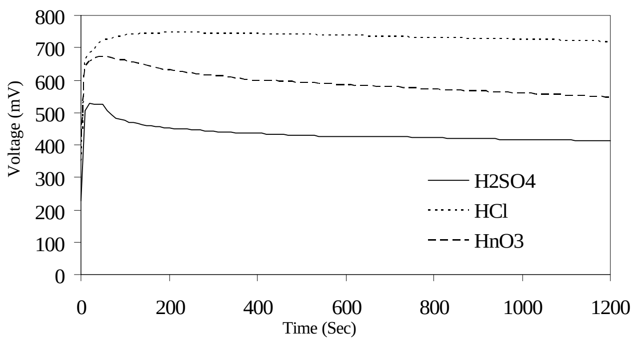

Figure 5. Chronopotentiogram recorded during electrochemical polymerization of 0·2 M concentration of aniline and 1 M concentration of H_2SO_4, HCl and HNO_3.

lifetime and fast response time. Polyaniline is one of the conducting polymers, which can be used to enhance the speed, sensitivity and selectivity of biosensors. The polyaniline have attracted more interest as a suitable matrix for entrapment of enzymes. The polyaniline is being used both as an immobilization matrix and as a physicochemical transducer to convert a chemical signal to electrical signal.

The chronopotentiogram recorded during electrochemical polymerization of PANI with different concentrations of aniline (0·1 M, 0·2 M, 0·3 M, 0·5 M) and 1 M concentration of H_2SO_4 is shown in figure 4.

It can be seen from figure 4 that 0·2 M concentration of aniline and 1 M concentration of H_2SO_4 have recorded lowest polymerization potential. The conductivity of synthesized PANI film with 0·2 M concentration of monomer and 1M concentration of H_2SO_4 was measured by four-probe technique. We have repeated the same experiment with 1M concentrations of supporting electrolytes, HCl and HNO_3. The chronopotentiogram recorded during electrochemical polymerization is as shown in figure 5. The conductivity of synthesized PANI film with 0·2 M concentration of aniline and 1 M of supporting electrolyte H_2SO_4, HCl and HNO_3 is shown in table 1. It can be seen from table 1 that the conductivity of synthesized PANI film is higher for H_2SO_4. Then we have synthesized PANI film with 0·2 M concentration of aniline and different concentrations of H_2SO_4 i.e. 0·5 M, 1 M and 1·5 M. The conductivity of synthesized PANI film with different concentrations of H_2SO_4 is as shown in table 2. It can be seen from table 2 that the conductivity of PANI is higher for 1 M concentration of H_2SO_4.

The voltage–current relationship of PANI film with 0·2 M concentration of aniline and 1 M concentration of H_2SO_4 is as shown in figure 6. The relationship between conductivity and temperature is illustrated in figure 7. The current (I) is set constant. It has been observed that as the temperature increases the conductivity increases; however, at higher temperature the conductivity of H_2SO_4 doped polyaniline films slow down significantly. The concept of conduction due to electron transfer in conduction band has been illustrated in figure 8. The conductivity of the polyaniline film synthesized by having 0·2 M of aniline and 1 M of H_2SO_4 shows an excellent conducting behaviour for the temperature ranges from 28–110°C. It is reported that the acidic doping of polyaniline results in partial protonation of nitrogen atom (Huang *et al* 1986; Karyakin *et al* 1994). Therefore, in this case the H_2SO_4 doping does not protonate the nitrogen completely in the polymer system.

Table 1. The conductivity of PANI films for 1 M concentration of electrolyte and 0·2 M concentration of aniline.

Electrolytes	Conductivity (S/cm)
H_2SO_4	0·7364
HCl	0·1315
HNO_3	0·0105

Table 2. The conductivity of PANI films for different concentrations of H_2SO_4 and 0·2 M concentration of aniline.

Electrolyte (in molar)	Conductivity (S/cm)
0·5	0·0610
1	0·7364
1·5	0·2762

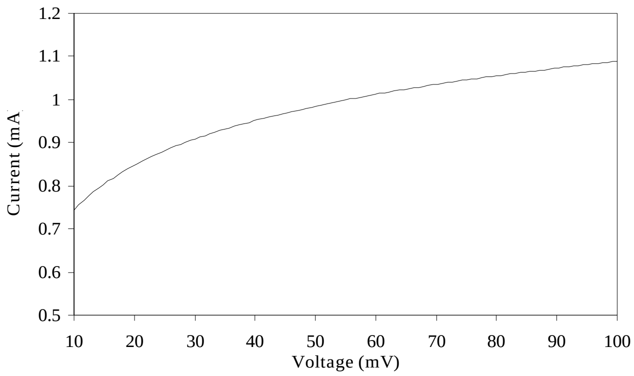

Figure 6. *I–V* curve of polyaniline sample.

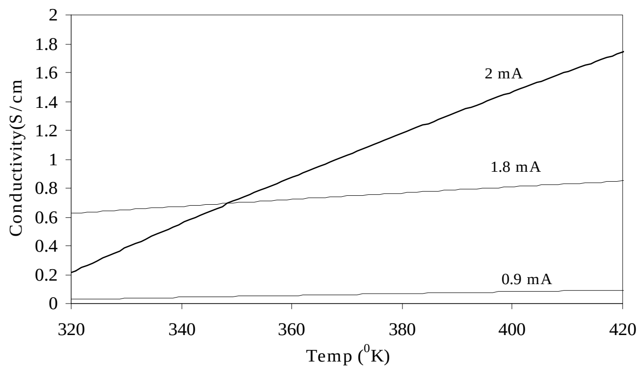

Figure 7. Temperature vs conductivity at different currents.

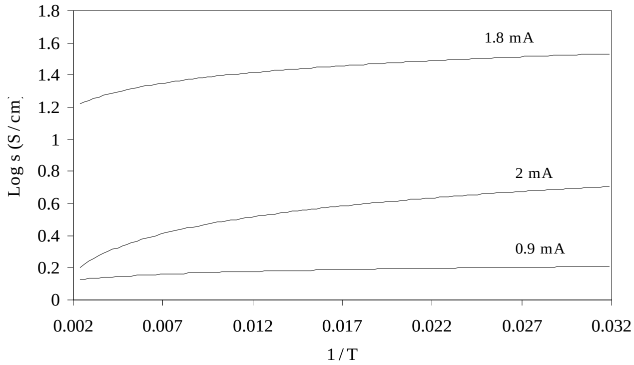

Figure 8. 1/T vs log s (S/cm) at different currents.

4. Conclusions

The four-probe technique provides an excellent method to measure the conductivity of H_2SO_4 doped polyaniline film. The PANI film with 0·2 M concentration of aniline and 1 M concentration of H_2SO_4 exhibits an excellent conducting behaviour.

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